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COMMENTS

Comment on “New Insight into Photochemistry of Ferrioxalate”

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In a recent paper,[1] Pozdnyakov et al. reported on the photochemistry of $[\mathrm{Fe^{III}(C_2O_4)_3}]^{3-}$ by means of flash photolysis and scavenging experiments. This paper has misinterpreted the results presented in a previous report[2] and consequently arrived at wrong conclusions. The data presented in ref 2 were used to propose the photoinduced electron transfer mechanism of ferrioxalate. This is an important addition to the photochemistry of this molecule and possibly others because it proposes that intramolecular electron transfer is not always the dominant process that occurs after excitation in the “charge transfer band”. On p 8318, Pozdnyakov et al.[1] stated that their “results [ref 1] are in disagreement with theoretical calculations [ref 2] predicting the maxima of absorption bands of $\mathrm{Fe^{III}(C_2O_4)_2}^-$ and $\mathrm{Fe^{II}(C_2O_4)_3}^{4-}$ at 430 and 400 nm, respectively. The reason is most probably due to neglect of solvation effects and spin orbital coupling in the theoretical calculations. Both factors seem to be taken into account for correct calculation of optical properties of such highly charged complexes of transient metals like oxalate complexes of Fe(II) and Fe(III) in a polar medium.” This statement is not correct because the data presented in ref 2 are strictly experimental and ref 2 does not present or even mention calculated transient spectra data. On the contrary, on p 9332, ref 2 presented time-resolved femtosecond to millisecond experimental data and stated “The observed spectra changes are assigned to reaction 3a, $\mathrm{Fe(III)(C_2O_4)_2}^-$ ($\lambda_{\max} = 430$ nm) to $\mathrm{Fe(II)(C_2O_4)_2}^{2-}$ ($\lambda_{\max} = 420-430$ nm)] and reaction 3b, the formation of $\mathrm{Fe(II)(C_2O_4)_3}^{4-}$ ($\lambda_{\max} = 400$ nm).” In contrast, ref 1 presents equilibrium steady state absorption measurements and suggests that these spectra are due to transient nonequilibrium species.

References1 and 2 have obtained different $\mathrm{CO_2}^{\bullet-}$ radical scavenging experimental data. The $\mathrm{CO_2}^{\bullet-}$ scavenger experiments are relevant because the intermolecular electron transfer mechanism proposed[2] generates $\mathrm{CO_2}^{\bullet-}$ radicals, which are responsible to some extent for the intermolecular electron transfer process. It should be noted that scavenging experiments involve complicated reactions; therefore, the results are usually not very accurate. For that reason, ref 2 used scavenging data only as a minor additional support for the proposed mechanism. The dominant results of ref 2 are picosecond time-resolved bond length changes measured by time-resolved EXAFS, supported strongly by DFT and UHF calculations and femtosecond time-resolved optical experiments.[2] The scavenger experiments performed by the two groups differ in the amount of $\mathrm{CO_2}^{\bullet-}$ radical scavenged. Reference 1 utilized $\mathrm{MV^{2+}}$ as the $\mathrm{CO_2}^{\bullet-}$ radical scavenger while ref 2 utilized thymine:

(a) $\mathrm{MV^{2+}}$ experiments: Pozdnyakov et al.[1] used $\mathrm{MV^{2+}}$ as the $\mathrm{CO_2}^{\bullet-}$ radical scavenger, excited with 355 nm pulses. On the basis of reactions 1 and 2 the yield of radical species (i.e., $\mathrm{CO_2}^{\bullet-}$ and $\mathrm{C_2O_4}^{\bullet-}$) generated was found to be less than 6% of the $[\mathrm{Fe^{III}(C_2O_4)_3}]^{3-}$ consumed.[1] The rate constants for the ferrioxalate/$\mathrm{CO_2}^{\bullet-}$ (k_3) and $\mathrm{MV^{2+}}$/$\mathrm{CO_2}^{\bullet-}$ (k_1) reactions are close to each other, within a factor of 2; therefore these two reactions closely compete with each other in scavenging $\mathrm{CO_2}^{\bullet-}$ to render the value of the $\mathrm{MV^{\bullet+}}$ reported[1] questionable. To completely quench the $\mathrm{CO_2}^{\bullet-}$ radicals, a high concentration $\mathrm{MV^{2+}}$ should be utilized. However, $\mathrm{MV^{2+}}$ has an absorption at 355 nm and, when irradiated at this wavelength, photochemistry is induced.[3,4] Therefore, use of $\mathrm{MV^{2+}}$ concentrations higher than 10^{-3} M is not valid. Also, the $\mathrm{MV^{\bullet+}}$/$\mathrm{C_2O_4}^{\bullet-}$ reaction rate constant (k_4) has been estimated to be 7×10^{10} $\mathrm{M^{-1}\ s^{-1}}$, around 7−20 times higher than the $\mathrm{MV^{\bullet+}}$ formation rate constants (k_1, k_2),[5] which may also greatly decrease the signal of $\mathrm{MV^{\bullet+}}$ and lead to very inaccurate conclusions.

$$\begin{array}{llll} \multicolumn{4}{l}{\mathrm{MV^{2+} + CO_2^{\bullet-} \rightarrow MV^{\bullet+} + CO_2}} \\ k_1 = 1.2 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}} & \text{(ionic strength = 0.1)} & \text{[ref 1]} & \\ k_1 \sim 7 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}} & \text{(ionic strength = 0.1)} & \text{[ref 5]} & (1) \\ k_1 = 1 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}} & \text{(zero ionic strength)} & \text{[ref 5]} & \end{array}$$

$$\mathrm{MV^{2+} + C_2O_4^{\bullet-} \rightarrow MV^{\bullet+} + 2CO_2} \qquad k_2 = (3.6 \pm 0.4) \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}\ \text{[ref 5]} \qquad (2)$$

$$\begin{array}{lll} \multicolumn{3}{l}{\mathrm{Fe^{III}(C_2O_4)_3^{3-} + CO_2^{\bullet-} \rightarrow Fe^{II}(C_2O_4)_3^{4-} + CO_2}} \\ k_3 = 5.5 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}} & \text{[ref 1]} & \\ k_3 = 4.0 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}} & \text{[ref 6]} & (3) \\ k_3 = 10^{9}-10^{10}\ \mathrm{M^{-1}\ s^{-1}} & \text{[refs 7 and 8]} & \end{array}$$

$$\mathrm{MV^{\bullet+} + C_2O_4^{\bullet-} \rightarrow MV^{2+} + C_2O_4^{2-}} \qquad k_4 = 7 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}\ \text{(estimated) [ref 5]} \qquad (4)$$

(b) Thymine experiments: we repeated the scavenger experiment reported in ref 2 using thymine as the $\mathrm{CO_2}^{\bullet-}$ radical scavenger. Considering the rather slow,[8,9] 5×10^4 $\mathrm{M^{-1}\ s^{-1}}$, reaction rate constant between thymine and $\mathrm{CO_2}^{\bullet-}$, high concentrations of thymine are needed to effectively quench $\mathrm{CO_2}^{\bullet-}$. Using 1.0×10^{-2} M thymine concentration, we found that the formation of the Fe(II) complex was decreased by more than 30%; see Figure 1. This suggests that the $\mathrm{CO_2}^{\bullet-}$ radical yield is similar to the “more than 50%” yield disclosed in ref 2 owning to the fact that even at these concentrations the $[\mathrm{Fe^{III}(C_2O_4)_3}]^{3-}$/$\mathrm{CO_2}^{\bullet-}$ reaction rate is orders of magnitude larger than the thymine/$\mathrm{CO_2}^{\bullet-}$ reaction rate.

Many intramolecular electron transfer and dissociation processes are known to occur in the 1−4 ps range. Reference 2 presents data that show dissociation occurs in this range and that support the mechanism proposed. However, ref 1 has not

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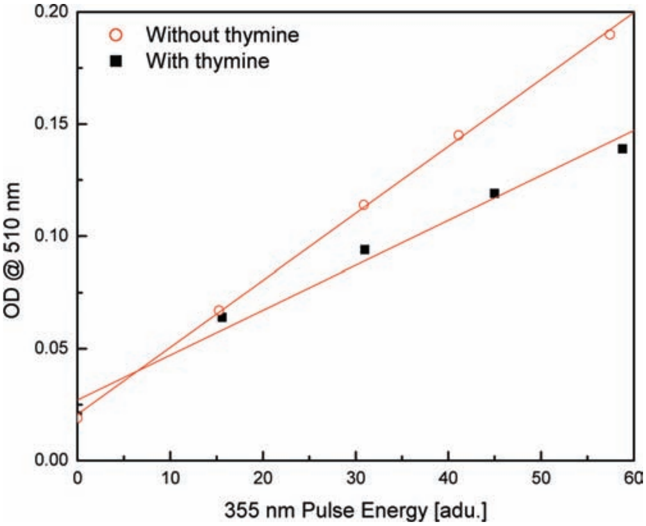

Figure 1. Optical density of the $[Fe^{II}(phen)_3]^{2+}$ complex at 510 nm plotted as a function of 355 nm pulse energy at the thymine concentration of zero (circle) and 1.0×10^{-2} M (square). The initial concentration of $[Fe^{III}(C_2O_4)_3]^{3-}$ is 6.5×10^{-5} M.

presented any time-resolved data in this time range. Also the ref 2 conclusion is based on picosecond time-resolved EXAFS and optical experimental data and DFT calculations while ref 1 neither shows any such data nor comments on these results.

References and Notes

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